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HYDROGEN PURIFICATION USING NATURAL ZEOLITE MEMBRANES

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ABSTRACT

The School of Science at Universidad del Turabo (UT) have a long-lasting investigation plan to study the hydrogen cleaning and purification technologies. We proposed a research project for the synthesis, phase analysis and porosity characterization of zeolite based ceramic perm-selective membranes for hydrogen cleaning to support NASA's commitment to achieving a broad-based research capability focusing on aerospace-related issues. The present study will focus on technology transfer by utilizing inorganic membranes for production of ultra-clean hydrogen for application in combustion. We tested 3 different natural zeolite membranes(different particle size at different temperatures and time of exposure). Our results show that the membranes exposed at 900°C for 1Hr has the most higher permeation capacity, indicated that our zeolite membranes has the capacity to permeate hydrogen.

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1. INTRODUCTION

The School of Science at Universidad del Turabo (UT), as part of a long-lasting investigation plan to study the viability of applying the plasma torch technology for hydrogen production from solid waste and also the development of integrated hydrogen cleaning technologies, proposes to develop a research project for the synthesis, phase analysis and porosity characterization of zeolite based ceramic perm-selective membranes for hydrogen cleaning to support NASA's commitment to achieving a broad-based research capability focusing on aerospace-related issues. The present study will focus on technology transfer by utilizing inorganic membranes for production of ultra-clean hydrogen for application in combustion. KSC will eventually be required to manufacture the hydrogen they use locally for reasons that include economics, transportation safety, and quantity requirements. The KSC spaceport hydrogen requirements will vary in the future, as they have in the past, due to fluctuations in launch activities, program changes, and other technical and weather-related factors. The development of perm-selective membranes for ultra-pure hydrogen production will, for example, result in increased efficiency of on-board fuel cells, thus reducing payload costs. NASA is interested in fuel cells that are light-weight, robust, and provide 2-20X more power density than the current state of art. Fuel cells can readily use pure hydrogen as a fuel source. Hydrogen has three main advantages relative to existing hydrocarbon fuels, i.e., no local air pollution, reduced oil consumption, and no greenhouse gas emissions.

Many industrial activities and other endeavors, such as combustion and fuel cells, require clean gases. Consequently, any effort to develop effective processes for gas cleanup is very useful. For example, an emerging new source of hydrogen gas comes from the pyrolysis of organic waste materials using a plasma arc torch [1-8], however, the hydrogen produced with this method is impure. Inorganic membranes are potentially very useful for gas separation and cleaning [9]. Microporous inorganic membranes are made of amorphous silica, carbon, and zeolites [10] and are potentially useful in gas separation for cleaning processes and in other areas, such as catalytic reactors, gasification of coal, water decomposition, and solid electrolyte fuel cells [10]. [11]. We used a combination of ceramic and sol-gel techniques to produce (synthesize) our natural zeolite membranes, it was characterized by Electronic Microscopy, X-Ray Diffraction, Elementary Analysis (EDAX) and Atomic Source Microscopy. Techniques.

Zeolites have been shown to be good adsorbents [18-27]. When a molecule diffuses inside a zeolite channel, it becomes attracted to and repelled by different interactions, such as the dispersion energy, repulsion energy, polarization energy, field dipole energy, field gradient quadrupole, sorbate-sorbate interactions [10, 23, 27-29] and the acid-base interaction with the active site if the zeolite contains hydroxyl bridge groups [27]. For the application of zeolites, the migration or diffusion of sorbed molecules through the pores and cages within the zeolite crystal plays a dominant role, *configurational diffusion* is the term coined to describe diffusion in zeolites

[20,22,23-25,30-33]. Free molecular transport generally occurs by ordinary diffusion such that Fick's laws are considered valid [30], however, single-file diffusion is also possible and very promising in membrane applications [34-38].

The diffusion of guest molecules through zeolite cavities and channels determines the molecular sieving properties of these materials [25,30,31,34,39,40]. Consequently it is possible to use zeolites based membranes for gas cleaning, since it is feasible, with the help of synthesis procedures, to control the pore size distribution of the obtained nano-structured materials in order to use its molecular sieving properties to selectively separate gases and as a result purify it. The most striking results in this field will be obtained in hydrogen cleaning, because of the small kinetic molecular diameter of the hydrogen molecule in comparison with the kinetic molecular diameters of the impurities [9-15,39].

Ceramic Technique:

If the zeolite temperature is increased to more than 500°C, after the dehydration, a phase transformation of the zeolite to a siliceous phase and a compact aluminosilicate phase occurs [41]. Moreover, if zeolite is ground and the powders obtained are sieved to obtain particles of grain size less than 100 µm, and if wafers are prepared with these fine particles by pressing at 100 MPa, after first agglomerating the powders with polyvinyl alcohol, and the wafers are thermally treated at 600, 700, 900, 1000, and 1150°C, an increase is observed in the density of the wafers from 1 g/cm³ at room temperature to 2.3 g/cm³ at 1150°C. As a result of a decrease of wafer porosity, ceramic materials are obtained that possess excellent mechanical properties [41] and also have a developed mesoporous structure [42]. Using the ceramic methodology, we have produced mesoporous ceramic membranes [42], these materials will be further transformed with the help of other methods, such as the sol-gel methodology, to obtain materials with micropores, that is, a pore distribution appropriate for hydrogen cleanup.

Sol-gel Method:

The hydrothermal synthesis of zeolites is carried out with highly reactive aluminosilicate gels under autogenous conditions [22]. The hydrothermal treatment of natural zeolites with highly basic sodium or potassium hydroxide solutions causes its amorphization and change in a chemical composition [29]. From our previous experience we know that it is possible to grow zeolite crystals over the surface of expanded clays [43,44], consequently we expect also to grow zeolite crystals over the produced mesoporous ceramic membranes in order to generate the microporous membrane. Thus, it is also proposed within the framework of the present project, to synthesize inorganic membranes with the help of the sol-gel method using the previously described zeolite-based mesoporous porous membranes [41-44] as support. The concrete sol-gel methodology that will be used for the hydrothermal treatment with a highly basic sodium solution [45] has been previously used by us for different purposes [29,45,46]

Porosity Characterization:

The analysis of isotherms of physical adsorption of gases and vapors represent a standard and conventional method for obtaining information about the pore structure of porous materials [18, 21, 28, 47-51]. During adsorption in complex systems, such as zeolites and related

materials, the adsorption process occurs as follows: initially, micropore filling (this means adsorption in the primary porosity, to be exact, pores with widths not exceeding about 2 nm) and afterward, at higher pressures, external surface coverage, consisting of monolayer and multilayer adsorption on the walls of mesopores (pores of width between 2 to 50 nm) and open macropores (pores of widths exceeding about 50 nm) and capillary condensation taking place on the walls of mesopores [18,21,38,47-49]. Adsorption in the primary porosity of zeolites is considered as a volume filling of the zeolite microporous adsorption space and not as a layer-by-layer surface coverage [51]. As is very well known, adsorption in the micropores is the principal method for the measurement of the microporous volume using the Dubinin adsorption isotherm [51], the t-plot method [18,21,47] and other adsorption isotherms [27]. On the other hand, capillary condensation of vapors is the primary method of assessment of the Pore Size Distribution (PSD) in the range of mesopores [18,21,28,48]. Capillary condensation is associated with a shift of the vapor-liquid coexistence in pores compared to bulk fluid, that is, a confined fluid in a pore condense at a pressure lower than the saturation pressure at a given temperature [48-50]. The condensation pressure depends on the pore size and shape and also on the strength of the interaction between the fluid and pore walls, consequently the adsorption isotherm allows to determine the PSD in the range of 2 to 50 nm [18, 21, 47-50]. During the last years the standard method for the determination of the PSD in the mesoporous range with the help of adsorption isotherms was the Barret-Joyner-Hallenda (BJH) method [18,48,50], however this methodology do not estimate properly the PSD [48,49]. Recently a new methodology of adsorption isotherm calculation based on the Non-Local Density Function Theory [48,49,52-54] which was originated in the Density Functional Theory applied to inhomogeneous fluids [55-57] have revolutionized the methodology of PSD calculation in microporous (less than 2 nm) and mesoporous materials (2 to 50 nm) [58]. This methodology is implemented in the Quantachrome Autosorb-1 Automated Surface Area and Pore Size Analyzer [58].

2. Methods and procedures

Clinoptilolite homoionization: A very well characterized natural zeolite [29] from the Sweetwater, Wyoming deposit [42,46] were refluxed five times for 1-3 hr. each in a 2M NaCl solution (liquid solid ratio = 2) at 373 K. The obtained samples were carefully washed with distilled water to produce the homoionized Na-clinoptilolite. The degree of Na⁺ exchange in the Na-clinoptilolite will be around 80-90 % [29,46].

Mesoporous zeolites based ceramics membranes synthesis: The homoionized sample were grounded, the sample obtained were sieved to obtain particles of grain sizes of $40 < \phi < 30$, $50 < \phi < 40$ and $100 < \phi < 50$. With these grains we prepared cylindrical wafers (10 mm x 0.5-1 mm) by pressing at 100 Mpa. The wafers were thermally treated at 700, 800 and 900°C during 1 and 2 hours.

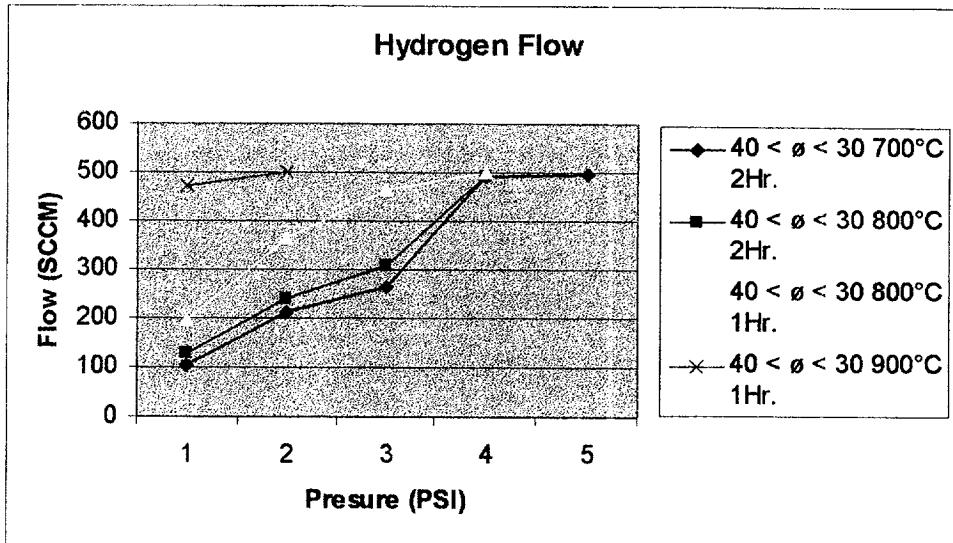
Phase analysis by XRD: The phase analysis of the transformation products and as-synthesized samples were determined using powder X-ray diffraction [61,62] in a Siemens powder diffractometer at the Materials Characterization Center at University of Puerto Rico-Rio Piedras Campus.

Electronic Scanning Microscopy: The synthesized samples was studied by SEM technique using a Scanning Microscope Model GOEL 5800LV and an elementary analysis by EDAX (DX4).

Pore size characterization by adsorption methods: We used the Quantachrome Autosorb-1 equipment to carry out the characterization of the pore structure of the produced membranes with the confidence that this is possibly the most reliable equipment in use worldwide among the research community for the characterization of the porous structure of porous materials [48,49,52-54,58]. Nevertheless, we will use also other methodologies, such as the t-plot method [18, 21,59] the Dubinin equation [51] and Langmuir and Fowler-Guggenheim Types Volume Filling Adsorption Isotherms [27] to test the validity of the new method used by the Autosorb-1 equipment employing the Ar and N₂ adsorption isotherms measured by the Autosorb-1 Surface Area and Pore Size Analyzer [58].

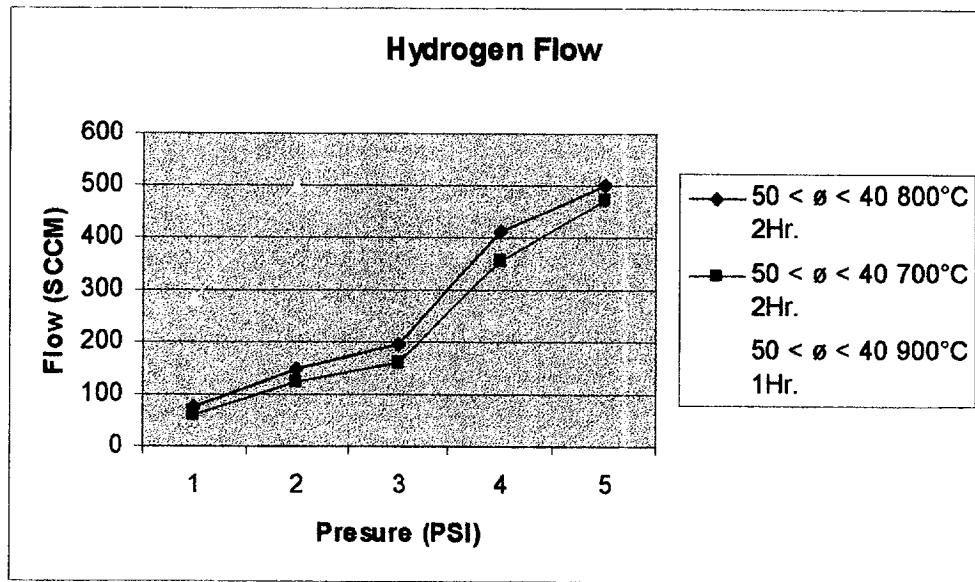
3. Results:

The zeolite membranes was placed into the gas system, the hydrogen(H₂) gas inlet pressures was 64.60, 79.60, 88.00, 127.60, 146.40, 197.20 and 208.80 PSI. The zeolite membranes of $40 < \phi < 30$, $50 < \phi < 40$ & $100 < \phi < 50$ 700, 800 & 900°C 1 & 2Hr results are showed in graphs 1,2 & 3. In graph 1, as you can see the most permeable membrane was $40 < \phi < 30$ 900°C 1Hr, were at 64.60 PSI the flow throught the membrane was 473.00 SCCM(Standard Cubic Centimeter per Minute) and the lowest permeation membrane was $40 < \phi < 30$ 700°C 2 Hr(at 64.60 PSI the flow was 104.00 SCCM). We found the same results with the $50 < \phi < 40$ 900 °C and $100 < \phi < 50$ 900 °C 1Hr(the highest permeability) and $50 < \phi < 40$ 700°C 2 Hr and $100 < \phi < 50$ 700°C 2 Hr (the lowest permeability)(see graphs 2 & 3). We also test the carbon dioxide(CO₂) permeability and we found that the membranes permit the CO₂ flow throught them and we found the same order, the most high permeability is on the membranes that was exposed at 900°C for 1Hr and the lowest permeability is on the membranes that was exposed at 700°C for 2 Hr. You can see in graphs 4, 5 & 6, the differences between the most high permeable membranes for hydrogen and carbon dioxide. The difference between them is around 2.00. The CO₂ permeation in this case is insignificant, that mean that the membranes have the capacity to permeate the Hydrogen.



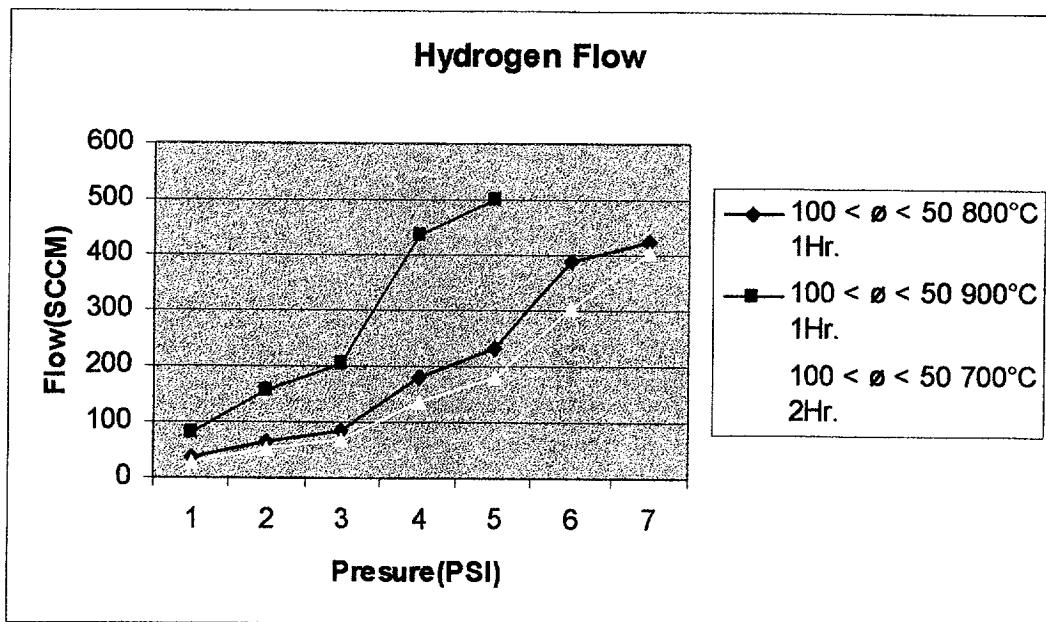
1 = 64.60 PSI, 2 = 79.60 PSI, 3 = 88.00 PSI, 4 = 127.60 PSI, 5 = 146.40 PSI

Graph 1: $40 < \phi > 30$ Membranes



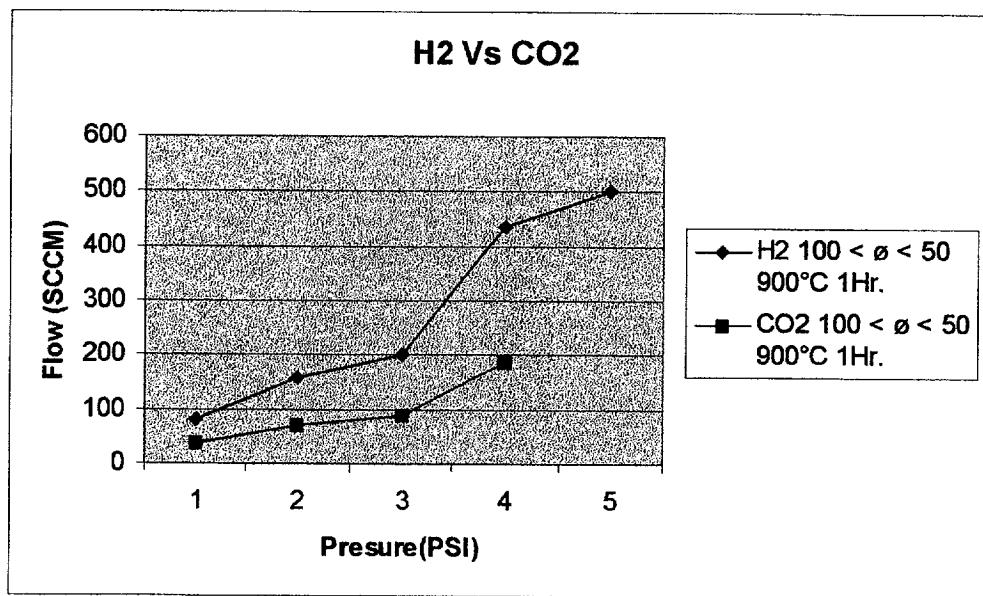
1 = 64.60 PSI, 2 = 79.60 PSI, 3 = 88.00 PSI, 4 = 127.60 PSI, 5 = 146.40 PSI

Graph 2: $50 < \phi < 40$ Membranes



1 = 64.60 PSI, 2 = 79.60 PSI, 3 = 88.00 PSI, 4 = 127.60 PSI, 5 = 146.40 PSI,
6 = 197.20 PSI, 7 = 208.80 PSI

Graph 3: $100 < \phi < 50$ Membranes



1 = 64.60 PSI, 2 = 79.60 PSI, 3 = 88.00 PSI, 4 = 127.60 PSI, 5 = 146.40 PSI

Graph 4: $100 < \phi < 50$ 900°C 1Hr Membranes Comparation